

QUARTERLY PROGRESS REPORT NO. 2

UPPER ATMOSPHERE CHEMICAL RELEASE STUDY

(1 Sept - 30 Nov 64)

NASw-985

Prepared by: Jerome Pressman

GEOPHYSICS CORPORATION OF AMERICA
Bedford, Massachusetts

For

National Aeronautics and Space Administration
Washington, D.C.

FACILITY FORM 802

N65-83831

(ACCESSION NUMBER)

13

(PAGES)

CR 622 25

(NASA CR OR TMX OR AD NUMBER)

(THRU)

None

(CODE)

(CATEGORY)

I. INTRODUCTION

In this quarterly, major emphasis has passed on to the experimental phase of the program. Several systems have been constructed for studying the relevant details of appropriate chemiluminescent reaction.

The chemiluminous titration of the upper atmosphere is an important technique for the elucidation of upper atmospheric parameters. However, there are only few studies⁽¹⁻⁴⁾ of chemiluminescent reactions which have been carried out with this point of view. The prime requisite, from the point of view of chemiluminous titration technique, is to observe the chemiluminescence under the conditions which are as close as possible to that of the upper atmosphere. Moreover, the same titrant should be simultaneously studied with major reactive constituents of the upper atmosphere. We are, at present, exploring the reactions of different compounds with atomic oxygen, ozone and atomic nitrogen.

II. EXPERIMENTAL APPARATUS

Two experimental arrangements have been completed for the present study:

1. Medium Pressure Flow Tube Apparatus - for surveying the reactions of different compounds.
2. Low Pressure Apparatus - for studying the light emission efficiency of suitable reactions.

A. MEDIUM PRESSURE FLOW TUBE APPARATUS

The apparatus used in the 500 μ or higher pressure region was of the fast flow reaction tube type and is shown in block diagrammatic form in Fig. 1.

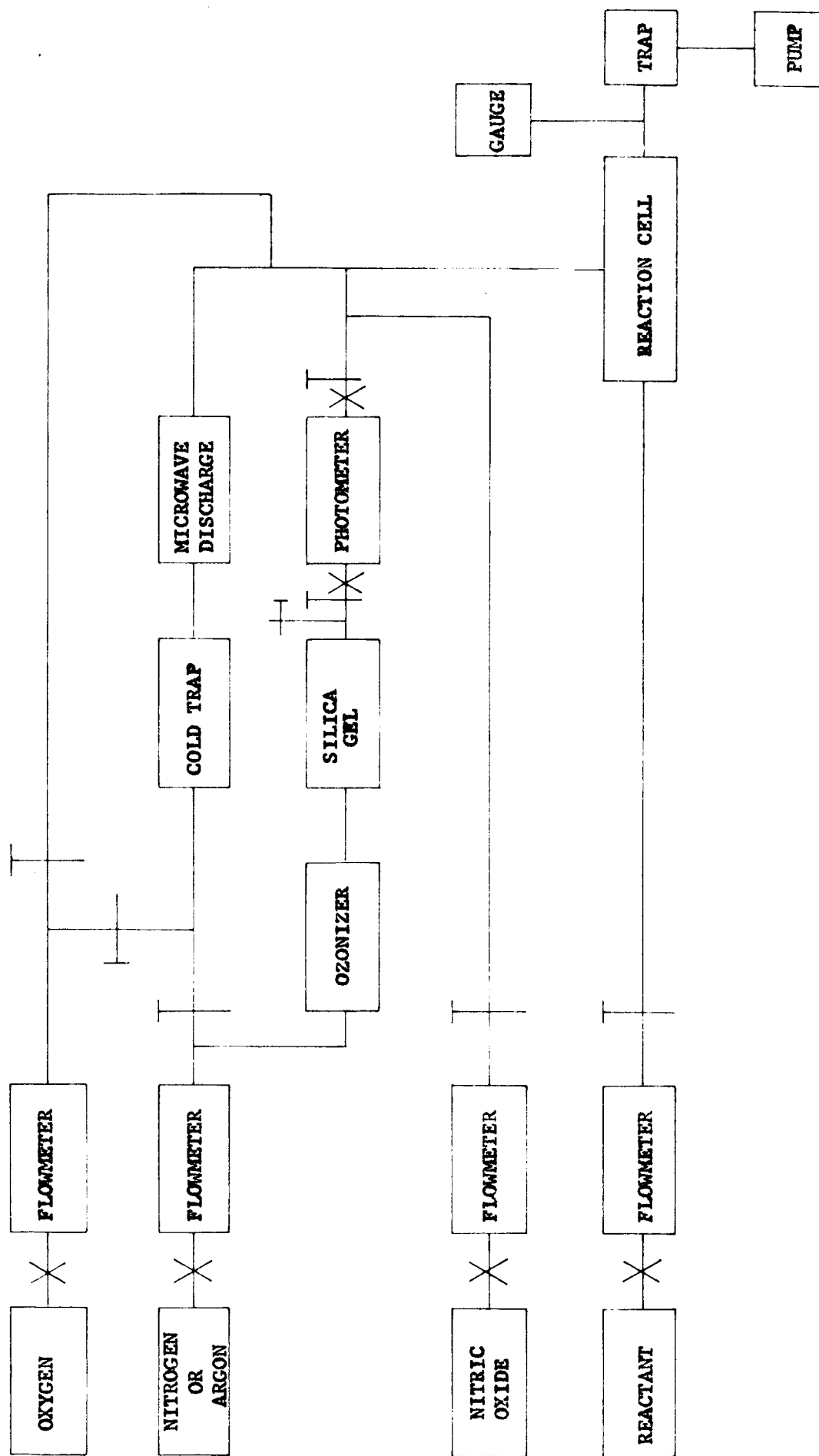


Figure 1. Medium pressure reaction system.

Using this system (with minor modifications) we could have: (1) atomic oxygen in the presence of molecular oxygen from microwave discharge through pure oxygen, (2) atomic oxygen with very little molecular oxygen by discharging a 99:1 mixture of argon and oxygen, (3) atomic oxygen in the absence of molecular oxygen by discharging nitrogen and titrating the N atoms thus focused with NO, (4) N-atoms from microwave discharge through nitrogen and (5) ozone. The ozone was prepared from silent discharge through flowing oxygen at atmospheric pressure and was adsorbed on silica gel at -80°C . Subsequently, the ozone system was connected with the vacuum system and ozone was desorbed at -30°C .

B. LOW PRESSURE APPARATUS

The system by which the atomic species and ozone are produced is the same as described above. The reaction cell was a 50-liter 3 necked Pyrex flask shown in Figure 2. It was continually evacuated by a large Welch mechanical pump (15 cft/min) and an N.R.C. 4 inch oil booster pump which has a maximum pumping efficiency between 1 and 100μ Hg. A liquid nitrogen baffle was maintained between cell and the booster pump. The pressure in the cell was measured by a McLeod gauge. It was found that no pressure gradient was set up in the reaction cell due to gas flows. In normal use the cell is coated by a layer of magnesium oxide in order to increase the light gathering efficiency.

C. EQUIPMENT

The spectrum of the chemiluminescent radiation was recorded when possible using a Perkin-Elmer single beam double pass spectrometer. Background noise was kept to a minimum by chopping the incoming light beam on its second pass at a fixed frequency of 13 cps.

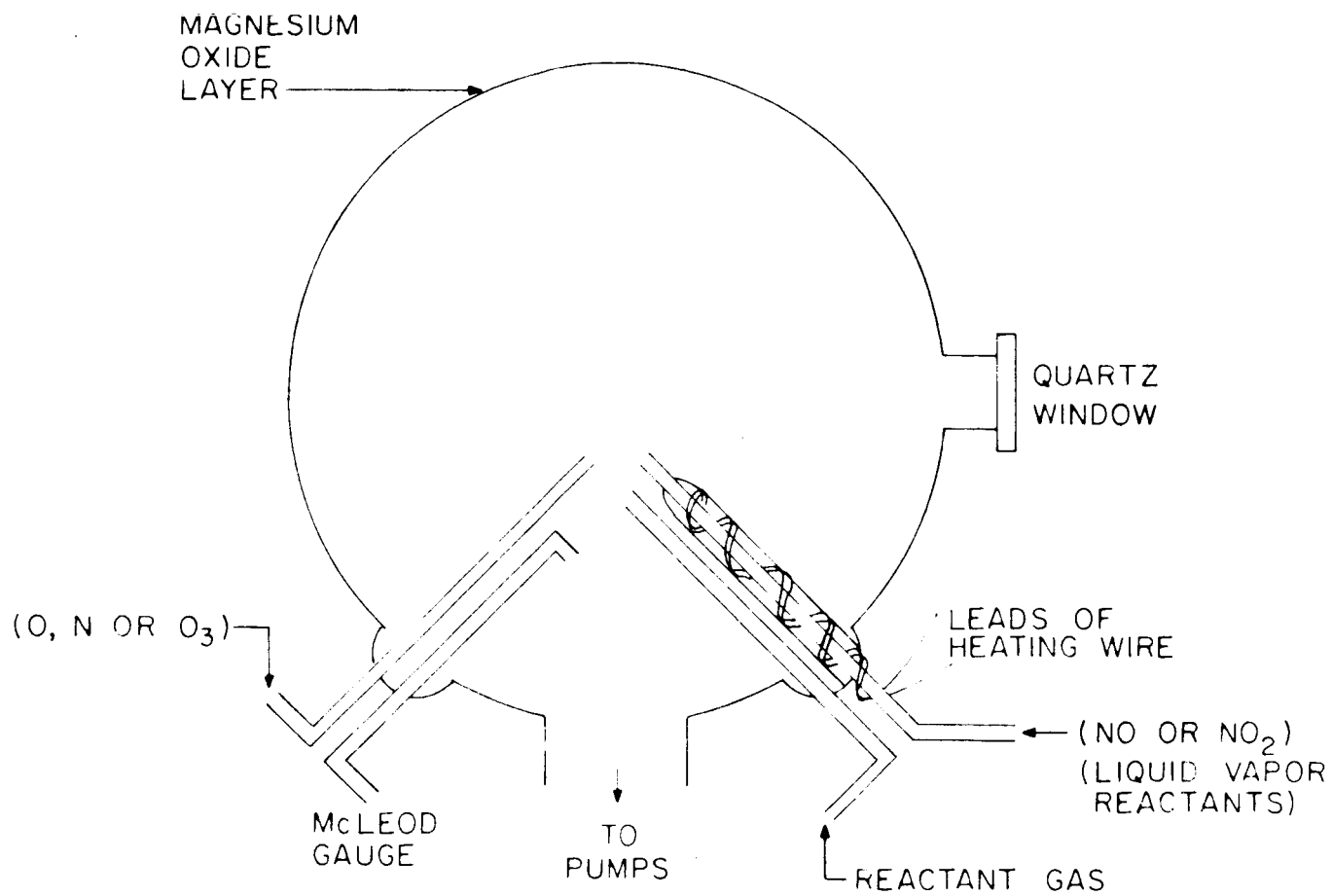


Figure 2. Low pressure reaction chamber.

The ac signal resulting at the detector was then fed into an amplifier tuned to this frequency. The spectra were recorded using a Leeds and a Northrup 10 millivolt recorder. The detector used was an E.M.I. 9558 Q photomultiplier tube fitted with a quartz window and S-20 response which can detect in the region 2500-7500 \AA . A special preamplifier was used to minimize electrical pick-up.

With the low pressure apparatus, it is desirable to measure the intensity of the over-all light emission. These measurements are made with either an RCA 1P28 photomultiplier tube (S5 cathode) or EMI 9558Q photomultiplier (S-20 cathode) couple with a victoreen microammeter.

The flow rates of atomic oxygen and nitrogen were determined by NO_2 and NO titration methods. Capillary flow meters were used for monitoring the flow of different gases. Fig. 3 shows the arrangement used to calibrate the different flow meters. The partial pressure of ozone was measured from the absorption of 2536.52 \AA Hg line through a 50 cm long tube with quartz windows. For this purpose a "Spectroline" Mercury Lamp with quartz envelope was used.

III. EXPERIMENTAL RESULTS

Several compounds have been selected for investigating their chemiluminescent reactions with atomic oxygen, nitrogen and the ozone molecule. Preliminary observations have been obtained on the reactions of acetylene and boron trichloride.

A. ACETYLENE

The reaction of acetylene with atomic oxygen has previously been studied⁽⁵⁾ in this laboratory. Kiess et al⁽⁶⁾ have reported the spectrum of the chemiluminescent reaction of acetylene with atomic nitrogen.

OICD48-3 OS

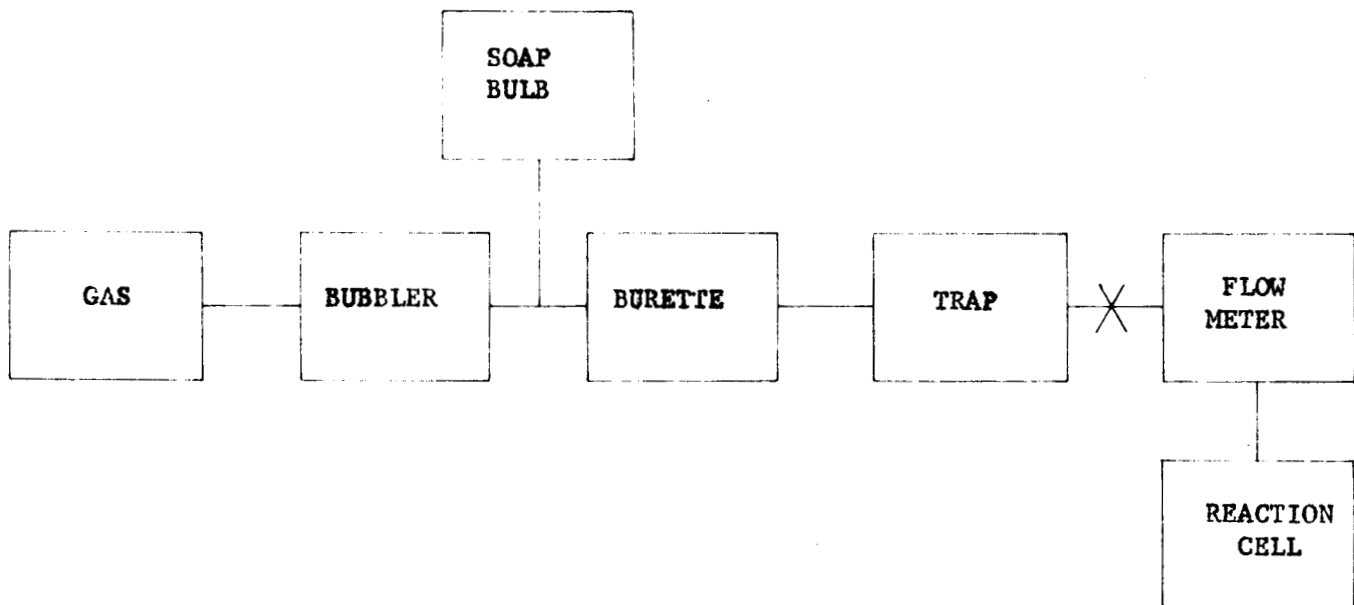


Figure 3. Experimental arrangement for calibrating flow meters.

Table 1 shows the spectral features of the reactions of acetylene with atomic nitrogen and atomic oxygen.

The reaction of ozone with acetylene was investigated as follows. Firstly, ozone was reacted with NO and the relative flows were adjusted to obtain the maximum red glow of the chemiluminescent reaction of O_3 with NO. The NO flow was stopped and then acetylene was introduced into system. The flow rates of acetylene and ozone were varied. It was found that under the present experimental conditions no visible radiation was observed due to the reaction of acetylene with ozone.

The spectral characteristics of the reaction of acetylene with N, O and O_3 are compared in Table 1.

TABLE 1

Spectral Feature ($\lambda, \text{\AA}$)	Reaction with O-atoms	Reaction with N-atoms	Reaction with O_3 -molecule
C_2 Swan Bands (25642-4362)	Observed	_____	_____
CH band (4300, 3900 or 3143)	Observed	_____	_____
OH-Ultraviolet System (3063-2833)	Observed	_____	_____
Continuum (6000-6500)	Observed	_____	_____
CN Violet System (4600-3600)	_____	Observed	_____
CN Red System (3000-4370)	_____	Observed	_____

In the absence of definite understanding of the mechanism for the excitation of spectral features, we can roughly estimate the chemiluminous efficiency of a reaction as follows:

$$\text{Chemiluminous efficiency} = \frac{I}{[R_1][R_2]}$$

where, I is the overall intensity of emission and $[R_1]$ and $[R_2]$ are the concentration of the two reactants in the reaction chamber. Thus, the chemiluminous efficiency of two reactions can be compared from the comparison of the intensity of radiation emitted under similar condition, i.e. pressure and concentration of reactants.

From the measurement of the intensity of CN and CH bands, emitted during the reaction of acetylene with N atoms and O atoms respectively, we have found that under similar experimental condition, the intensity of CN bands is about sixty times less than that of CH bands. Since the concentration of the nitrogen atoms is lower than that of the oxygen atoms in the upper atmosphere, it may be concluded that the chemiluminous reaction of acetylene with nitrogen atoms should not appreciably affect the chemiluminous titration of O atoms by acetylene.

B. BORON TRICHLORIDE

The reaction of boron trichloride with atomic nitrogen, oxygen and ozone was investigated.

The nitrogen atoms were produced by the usual method of microwave discharge from commercial nitrogen without purification. The flow rates of N atoms in the reaction tube was about 1.5 cc/min. On introducing the BCl_3 vapor in the reaction tube, it was found that the N_2 afterglow was replaced by a faint green glow.

In addition to the faint bands of N_2 afterglow, the spectrum of the glow produced by boron trichloride and active nitrogen consists of the bands of BO and BO_2 molecules. Mulliken⁽⁷⁾ has also observed BO bands in the spectrum of the glow produced by the reaction of active nitrogen with boron trichloride. It appears that the oxygen present as an impurity in the tank nitrogen plays an important role in the excitation of the chemiluminescence. Therefore, the reaction of BCl_3 with atomic oxygen was investigated. In the study of the reaction with atomic oxygen in the presence of molecular oxygen, the spectrum of the glow consists mainly of BO_2 bands together with a few faint bands of BO. However, the spectrum of the glow produced by the reaction of boron trichloride with atomic oxygen in the virtual absence of molecular oxygen shows bands of BO_2 and BO molecules. The relative intensity of the BO bands in comparison with that of the BO_2 is greater when molecular oxygen is absent than when it is present.

The low intensity of the chemiluminescence produced in the above reactions required a wide slit of the spectrometer for the recording of the spectrum. Therefore, the definite identification of all the peaks recorded in the spectra was not possible. However, the wavelength and the relative intensity of the peaks recorded in the spectra are given in Table II. The tentative identification is also shown in the same table.

No visible chemiluminescence was observed during the reaction of boron trichloride with ozone.

C. SURVEY OF CHEMILUMINOUS REACTIONS OF OZONE

The reactions of several compounds with ozone have been surveyed up to 500 μ pressure, with different flow rates of ozone and other reactants. The reactions of ozone with methyl acetylene, allene, ethylene, nitric oxide, carbonyl sulphide and nitrosyl chloride were investigated. It has been found that except for nitric oxide and ethylene, none of the above compounds shows visible chemiluminous reactions with ozone, under the present experimental condition. The intensity of glow produced by nitric oxide and ethylene was very feeble. Therefore, the spectra of the glow could not be recorded. The color of the glow produced by NO with ozone is red and that of ethylene with ozone is greyish white.

IV. FUTURE PLANS

With the two apparatus constructed and several compounds checked out, the next quarter will see the checking of a priori estimated optimal compounds for measuring active components of the upper atmosphere. The theoretical work will continue.

TABLE 2

Observed Peak $\lambda(\text{\AA})$	Probable Identification	Relative* Intensity (Atomic Nitrogen)	Relative* Intensity (Atomic Oxygen with Molecular Oxygen)	Relative* Intensity (Atomic Oxygen in Absence of Molecular Oxygen)
6656	N ₂ , 1P, (6,3)	0.5	—	—
6500	N ₂ , 1P, (7,4)	0.5	—	—
6328	N ₂ , 1P, (10,7)	1	—	—
6141	BO, (0,4)	1	—	—
6006	BO ₂	1.5	1	1.5
5863	N ₂ , 1P, (10,6)	1.5	—	—
5772	BO ₂	2	3	2.5
5590	N ₂ , 1P, (6,1)	1.5	—	—
5538	BO, (0,3)	2.5	—	4
5434	BO ₂	—	3	6
5369	N ₂ , 1P, (12,7)	2	—	—
5252	BO ₂	1.5	—	—
5153	BO ₂	2	10	8
5036	BO, (0,2)	2	—	7.5
4906	BO ₂	1.5	7	10
4742	BO, (1,2)	1.5	—	—
4703	BO ₂	—	5	10
4638	BO, (0,1)	2	—	8
4508	BO ₂	—	3	6.5
4339	BO, (1,1)	2	1.5	7
4144	BO, (2,1)	3	1	4
4040	BO, (1,0)	1.5	—	5
3850	BO, (2,0)	10	—	2.5
3686	BO, (3,0)	—	—	1
3522	BO, (4,0)	1.5	—	1

*The relative intensity given in columns 3-5 are correct for the same column only and can not compare with two different columns.

References

1. Jonathan, N. and Doherty, G., NASA Report No. CR-67 by Geophysics Corporation of America, Bedford, Mass. (1964)
2. Jonathan, N. and Doherty, G., "Planetary Aeronomy IX = The Dark Side Airglow of Venus," GCA Technical Report 63-1-N. Contract No. NASw-395 (1963)
3. Fontijn, A. and Schiff, H. I., Chemical Reactions in the Upper and Lower Atmosphere. Interscience Publications (1961)
4. Reeves, R. R., Harteck, P. and Chance, W. H., J. Chem. Phys., 41, 764 (1964)
5. Jonathan, N. and Warneck, P., "Continuation of Laboratory Chemiluminescent Experiments for Ballistic Missile Defense," GCA Technical Report No. 64-12-A Final Report, Contract No. AF19 (628)-3320. Geophysics Corporation of America, Bedford, Mass. (1964)
6. Kiess, N. H. and Broida, H. P., Seventh Symposium of Combustion, Butterworth Scientific Publications, (1959).
7. Mulliken, R. S., Phys. Rev., 25, 259, (1925)